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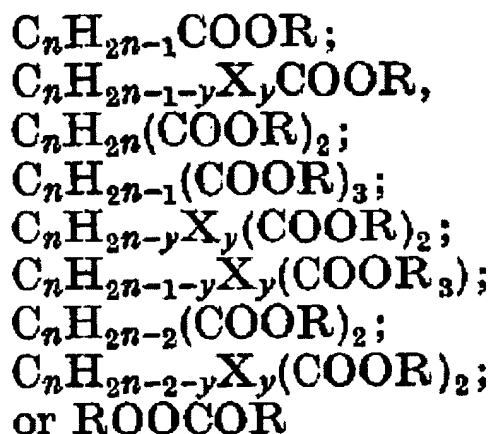
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Abstract of GB1217709

1,217,709. Curing polymers by laser beam. FMC CORP. 13 Sept., 1968 [14 Sept., 1967], No. 43570/68. Heading C3P. [Also in Division G2]
 Resins compositions which are curable by laser beams comprise a thermally cross-linkable allylic ester resin obtained by the polymerization of an addition polymerizable allyl carboxylic ester having a plurality of aliphatic ethylenically unsaturated linkages, at least one of which is an allyl ester group, the resin having residual unsaturation and being a solvent-soluble material which is a solid at ambient temperatures and which undergoes very little shrinkage when further polymerized by heat at room temperature; and a peroxide catalyst which accelerates polymerization of the said cross-linkable allylic ester resin. Preferred resins are (A) prepolymers of esters of formul : (in which R is allyl, n is 1-17, y is 1 or 2, and X is halogen, OH, optionally substituted phenyl, furfuryl or C 1-4 alkyl or alkoxy); (B) copolymers of (i) an allyl ester of an unsaturated monobasic acid or (ii) a poly(allyl) ester of an aliphatic carboxylic acid, with another monomer (e.g. butadiene, styrene, methylmethacrylate, vinylidene chloride, vinyl chloride, vinyl acetate, diethylene glycol, maleate, cinnamyl cinnamate) and (C) polymers of allyl esters of benzene, naphthalene and s-triazine carboxylic acids.



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NO DRAWINGS

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 4P6H 4P6X 4T2A 7D2A1 7K4 7K8 7P1E3 7P3
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 9P5 9P6D 9P6G 9P6H 9P6X 9T2A

G2M



(54) PRINTING PLATES

(71) We, FMC CORPORATION, a Corporation incorporated in the State of Delaware, United States of America, of 633, Third Avenue, New York, State of New York, United States of America, (Assignee of LEO SETH BURNETT), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of heat-cured resin images useful as printing surfaces by means of modulated laser radiation.

It is well known in the photomechanical art to form printing surfaces by the action of actinic radiation on photosensitive materials. The usual procedure consists of exposing to a light pattern a layer of the photosensitive material which becomes hardened and insoluble where irradiated. After removing the unaltered coating in the unexposed areas, there remains a hardened area corresponding to the light pattern. The photosensitive material is commonly a resinous substance which undergoes crosslinking in the presence of actinic radiation thereby becoming toughened and insoluble. Among the earliest photosensitive materials of this type, and still being used, are the bichromated colloids as exemplified by gum arabic, gelatin, albumin and the like. In recent years the use of photopolymerizable compositions has received a good deal of attention. These consist of a mixture of a photosensitizer and an ethylenically unsaturated compound which polymerizes when exposed to light in the presence of the sensitizer. The resulting photopolymerized images are then employed as printing surfaces.

The ethylenically unsaturated compound can be a monomer or a partially polymerized material capable of undergoing further polymerization in the presence of actinic light.

The present invention is an improvement in the photolithographic art, providing a new technique for producing printing plates in which polymeric or resinous printing surfaces are formed by focusing a modulated laser beam or pattern on a heat-hardenable material applied as a coating to a base plate. The heat generated by the laser where it impinges on the coating brings about a local hardening and insolubilization.

According to the present invention, there is provided a method for the production of a planographic printing plate which comprises (1) coating a base material with a thermally crosslinkable allylic ester resin obtained by the polymerization of an addition polymerizable allyl carboxylic ester having a plurality of aliphatic ethylenically unsaturated linkages, at least one of which is an allyl ester group, the resin having residual unsaturation and being a solvent-soluble material which is a solid at ambient temperatures and which undergoes very little shrinkage when further polymerized by heat at ambient temperature; and a peroxide catalyst which accelerates polymerization of the said crosslinkable allylic ester resin; (2) exposing the coating to a modulated laser beam or pattern which generates heat where it contacts the coating thereby forming a hardened polymerized image; (3) developing the coating to remove the unhardened portions thereof, leaving the polymerized image intact.

The expression "which undergoes very little shrinkage when further polymerized by heat at room temperature" means that the area of the light hardenable, photosensitive

coating must not change during photopolymerization and subsequent processing of the exposed plate. Such dimensional stability is essential in order to obtain a photopolymeric image, which constitutes a true replica of the original light pattern, and from which distortion free printed copies can be realised. Those portions thereof receiving little or no exposure from the laser may be dissolved away by applying a solvent to the irradiated coating leaving a hardened resinous image where exposure occurred and the resulting plate may be desensitized in the usual manner after which it can be inked and used to prepare printed copies. An offset printing press is a convenient apparatus for producing printed copies.

Various types of signals can be used to modulate the laser beam for subsequent conversion into a visible record in accordance with the invention. For instance, printed characters can be scanned and converted into electrical impulses which serve as a signal for superimposition on the laser carrier. In fact, the present invention makes possible the production of printing plates directly without the necessity of type setting. The manuscript characters and letters are electronically scanned and the resulting signal impressed on the laser beam which in turn is directed against a heat-hardenable coating in the manner described herein thereby forming manuscript characters of cured polymer which is then converted to a printing plate from which copies are then made corresponding to the original scanned manuscript. Other signal sources, such as the outputs from computers and television transmitters, can be converted to printing surfaces for making visible records by the procedure of the invention.

Laser generators are well known in the electronic arts and their description and construction is detailed in the technical literature. In order that the images produced by the process herein have a high degree of resolution, the laser beam should have a relatively small cross-sectional area; on the order of a few microns.

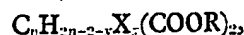
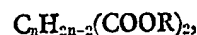
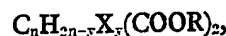
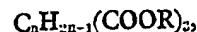
Exemplary allylic ester resin materials are illustrated in the following list:

(a) Prepolymers derived from allyl esters of unsaturated monobasic acids having either the general formula $C_nH_{2n-1}COOR$ or $C_nH_{2n-1-y}X_yCOOR$, such as allyl acrylate, allyl chloroacrylate, allyl methacrylate, allyl crotonate, allyl cinnamate, and allyl furfurylacrylate. It is to be understood that in all formulas used herein, R is an allyl group, n can be any integer from 1 to 17 inclusive, except where the acid is unsaturated in which case n is 2 to 17, y is 1 or 2, and X is a halogen, hydroxyl, phenyl, substituted phenyl or furfuryl group or an alkyl or alkoxy group having 1—4 carbon atoms.

(b) Prepolymers of allyl esters of un-

saturated monobasic acids; such as allyl methacrylate with butadiene, allyl methacrylate with methyl methacrylate, allyl methacrylate with styrene, allyl methacrylate with vinylidene chloride, allyl crotonate with methyl methacrylate, allyl crotonate with styrene, allyl crotonate with vinyl chloride, allyl crotonate with vinyl acetate, allyl crotonate with vinylidene chloride, allyl crotonate with diethyleneglycol maleate, allyl cinnamate with vinylidene chloride, allyl cinnamate with styrene and allyl cinnamate with cinnamyl cinnamate.

(c) Prepolymers derived from allyl esters of aliphatic carboxylic acids, said esters having two or more allyl groups and having one of the following general formulae:



or



such as diallyl malonate, diallyl succinate, diallyl sebacate, diallyl maleate, diallyl fumarate, diallyl itaconate, diallyl tartrate, diallyl carbonate, diallyl adipate, triallyl citrate, diallyl malate and diallyl citraconate.

(d) Precopolymers of allyl esters of aliphatic carboxylic acids, said esters having two or more allyl groups, such as diallyl oxalate with vinylidene chloride, diallyl oxalate with styrene, diallyl malonate with vinylidene chloride, diallyl succinate with vinylacetate, diallyl succinate with vinylidene chloride, diallyl succinate with polyvinyl acetate, diallyl adipate with vinylidene chloride, diallyl sebacate with vinylidene chloride, diallyl maleate with methyl methacrylate, diallyl maleate with styrene, diallyl maleate with vinylidene chloride, and diallyl carbonate with methyl methacrylate.

Particularly useful are the diallyl phthalate resins.

In the aromatic series are those crosslinkable copolymer resins derived from allyl esters in which the acid is normally of the benzene and naphthalene series, typical monomers being diallyl isophthalate, diallyl terephthalate, triallyl mellitate, and tetraallyl pyromellitate.

In the manufacture of crosslinkable allylic ester resins, also known as prepolymers, the monomeric materials are polymerized in con-

ventional fashion to produce a solution of a soluble polymer in the monomer to the point short of gelation which occurs when the molecular weight of the polymer approaches that point where it becomes insoluble in the monomer. These polymer solutions, or dopes, are then separated into a solvent-soluble prepolymer fraction and a monomer fraction. This is effected by treatment with a solvent which dissolves the monomer while precipitating the polymerized portion or by other means which will leave a soluble prepolymer substantially free of monomer. A typical method for separating such crosslinkable prepolymers is described in U.S. Patent 3,030,341.

The crosslinkable allylic ester resins of the invention used with a peroxide catalyst and in this connection reference is made to hydrogen peroxide, aliphatic hydroperoxides such as methyl hydroperoxide, ethyl hydroperoxide, t-butyl hydroperoxide, hexyl hydroperoxide, octyl hydroperoxide, transdecalin hydroperoxide, 1-methylcyclopentyl hydroperoxide, 1,1-dimethyl-2-propenyl hydroperoxide, 2-cyclohexene-1-yl hydroperoxide, cumene hydroperoxide, tetralin hydroperoxide and triphenyl-methyl hydroperoxide; peroxides of the formula ROOR' wherein R and R', which may or may not be alike, can be alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl and undecyl; aralkyl such as benzyl, phenethyl, phenylpropyl, naphthylethyl, naphthylmethyl and naphthylpropyl; aryl such as phenyl and naphthyl; aliphatic acyl such as acetyl, propionyl, butyryl and valeryl; aromatic acyl such as benzoyl and naphthoyl; peroxy acids, including aliphatic peroxy acids such as peracetic acid, perpropionic acid and perbutyric acid and aromatic peroxy acids such as perbenzoic acid and perphthalic acid; esters of the aforesaid peroxy acids; salts of peracids such as ammonium persulfate. Such compounds are well known and their description and preparation can be found in the chemical literature. An especially informative treatise is the well-known "Organic Peroxides", by Arthur V. Tobolsky and Robert B. Mesrobian, and published by Interscience Publishers, Inc. New York, and Interscience Publishers, Ltd., London (1954).

Any suitable amount of catalyst may be used but, in general, it is used in the range of about 0.1 to about 6.0% by weight of the resin; dicumyl peroxide, tert.-butyl perbenzoate and tert.-butyl hydroperoxide are preferred examples.

The mixture of peroxide catalyst and crosslinkable allylic ester resin is conveniently coated on a metal base plate such as aluminum or chromium plated steel or other oleophobic metal. It is preferable to use aluminum sheet since it is relatively inexpensive, has the requisite structural rigidity and is readily desensitized to present a non-

inking or oleophobic surface. Those skilled in the art will select that particular combination of base materials which best suits their own particular needs.

The liquids used to remove or dissolve the non-hardened allylic ester resin film in the unexposed areas are advantageously relatively high-boiling organic solvents of the type commonly employed in most lithographic shops. One preferred solvent is tris-(tetrahydrofurfuryl) phosphate although excellent solvents include aromatic hydrocarbons and their chlorinated derivatives such as toluene, xylene, chlorinated xylene and chlorinated toluene; aliphatic hydrocarbons and chlorinated derivatives thereof, for example, trichloroethylene and trichloroethane; also high boiling ketones and the glycol ether esters such as esters of ethylene glycol monoethyl ether (Cellosolve) and esters of diethylene glycol monethyl ether (Carbitol). "Cellosolve" and "Carbitol" are Trade Marks. Such solvents can be used alone or in mixed combinations or as emulsions in water.

The invention is illustrated by the following non-limiting examples.

EXAMPLE 1

A heat crosslinkable coating solution suitable for preparing the printing plates of the invention is prepared as follows:

12.0 g of diallyl isophthalate prepolymer	
88.0 g of Pent-Oxone ("Pent-Oxone" is a Trade Mark for 4 - methoxy-4 - methylpentanone - 2)	
0.5 g of dicumyl peroxide	100

The prepolymer and dicumyl peroxide are dissolved in the pentoxone and the solution filtered to remove insoluble fraction. In some instances, purification is best effected by centrifuging.

The coating is then applied using a whirl coater onto a grained aluminum sheet so as to produce a uniform layer having a thickness of 0.1 mil. After evaporation of some of the solvent, the plate is then heated to 125°F for 5 minutes to remove most of the residual solvent. After cooling, the coating appears as a dry film on the aluminum substrate. The plate is next exposed to a modulated laser beam whereby the heat generated by the laser beam causes the coating to crosslink or cure in the exposed areas thereby forming insoluble and toughened surfaces. Development of the irradiated plate is effected by immersion in xylene to remove the unhardened or unpolymerized resin corresponding to the non-image portions thereby leaving the aluminum base plate covered in the image areas but bared in the non-image areas. Next, a desensitizing phosphoric gum etch, of the type commonly used in the art, is applied in order to render the aluminum

non-image areas hydrophilic, or water receptive, and thereby repellent to printing ink. The developed plate can then be inserted in an offset printing press and printed copies run off.

The plates produced in accordance with the aforescribed Example are long-running, being capable of producing on the order of 100,000 to 300,000 impressions.

The procedure of Example 1 is repeated except that the following coating solutions are used:

EXAMPLE 2

1.5 g allyl methacrylate prepolymer
2.5 g methyl isobutyl ketone
2.5 g Cellosolve acetate
.03 g dicumyl peroxide

EXAMPLE 3

1.5 g prepolymer of a copolymer of allyl cinnamate with styrene
2.0 g methyl isobutyl ketone
2.0 g xylene
1.0 g Cellosolve acetate
.05 g tert.-butyl peroxide

EXAMPLE 4

1.5 g diallyl succinate prepolymer
5.0 g methyl isoamyl ketone
.04 g tert.-butyl peroxide

EXAMPLE 5

1.5 g prepolymer of a copolymer of diallyl maleate with methyl methacrylate
5.0 g Cellosolve acetate
.04 g tert.-butyl peroxide

EXAMPLE 6

1.5 g diallyl maleate prepolymer
5.0 g methyl isoamyl ketone
.04 g tert.-butyl peroxide

WHAT WE CLAIM IS:—

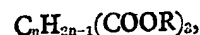
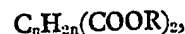
1. A method for the production of a planographic printing plate which comprises (1) coating a base material with a thermally crosslinkable allylic ester resin obtained by the polymerization of an addition polymerizable allyl carboxylic ester having a plurality of aliphatic ethylenically unsaturated linkages, at least one of which is an allyl ester group, the resin having residual unsaturation and being a solvent-soluble material which is a solid at ambient temperatures and which undergoes very little shrinkage when further polymerized by heat at ambient temperature; and a peroxide catalyst which accelerates polymerization of the said crosslinkable allylic ester resin; (2) exposing the coating to a modulated laser beam or pattern which generates heat where it contacts the coating thereby forming a hardened polymerized image; (3) developing the coating to remove

the unhardened portions thereof, leaving the polymerized image intact.

2. A method as claimed in claim 1 in which the allylic ester resin is a prepolymer derived from an allyl ester of an unsaturated monobasic acid having the general formula $C_nH_{2n-1}COOR$ or $C_nH_{2n-1-y}X_yCOOR$ wherein R is an allyl group, n is an integer from 1 to 17 except where the acid is unsaturated in which case n is 2 to 17, y is 1 or 2 and X is halogen, a hydroxyl, phenyl, substituted phenyl, or furfuryl group, or an alkyl or alkoxy group having 1 to 4 carbon atoms.

3. A method as claimed in claim 1 in which the allylic ester resin is a precopolymer of an allyl ester of an unsaturated monobasic acid.

4. A method as claimed in claim 1 in which the allylic ester resin is a prepolymer derived from an allyl ester of an aliphatic carboxylic acid, said ester having two or more allyl groups and having one of the formulae:



or



wherein R, X, n and y are as defined in claim 2.

5. A method as claimed in claim 1 in which the allylic ester resin is a precopolymer of an allyl ester of an aliphatic carboxylic acid, said ester having two or more allyl groups.

6. A method as claimed in claim 1 in which the allylic ester resin is derived from an allyl ester the acid of which is of the benzene or naphthalene series.

7. A method as claimed in claim 6 in which the allylic ester resin is a diallyl phthalate resin.

8. A method as claimed in any of claims 1 to 7 in which the base material is aluminum.

9. A method as claimed in any of claims 1 to 8 in which the catalyst is employed in an amount of 0.1 to 6.0% by weight based on the resin.

10. A method as claimed in any of claims 1 to 9 in which the catalyst is dicumyl peroxide, tert-butylperbenzoate or tert-butylhydroperoxide.

11. A method according to claim 1 substantially as hereinbefore described with par-

particular reference to any of the foregoing
Examples.

12. A planographic printing plate whenever
obtained by a method as herein described and
5 claimed.

W. P. THOMPSON & CO.,
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